15TH GROUP ELEMENTS

- Called Pnicogens as they cause suffocation.

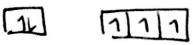
$_{7}N$	$[He]\ 2s^2\ 2p^3$
$_{15}P$	$[Ne]\ 3s^2\ 3p^3$
$_{33}As$	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$
$_{52}Sb$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^3$
$_{83}Bi$	$[Xe]\ 4f_2\ 5d^{10}\ 6s^2\ 6p^3$

Compounds are sublimable

As is sublimable

As & Sb compounds are sublimable

- GEC: $ns^2\ np^3$



These elements are fairly stable on account of half-filled p-subshells.

General Properties

1. Physical state:

N → gas

P → waxy solid

As, Sb, Bi → solids

2. Metallic nature

N, P → Non metal

As, Sb → Metalloids

Bi → pure metal

3. Atomic radius :

(Covalent radius)

$N \xrightarrow{Inc} Bi$

$N \xrightarrow[inc]{Expected} P \xrightarrow[inc.]{less} Bi$

(poor screening effect of d & f e^-)

- From N to P, the increase in size is as much as expected.
- Thereafter, the increase in size is less

Reason:

Poor screening effect of d e^- on As, Sb & d & f e^- in Bi

4. Ionic radius

$(Sb^{+3} < Bi^{+3}) < (N^{3-} < P^{3-} < As^{3-})$

5. IP :

$N \xrightarrow{Dec} Bi$

$N \xrightarrow[dec]{Expected} P \xrightarrow[dec.]{less} Bi$

- From N to P, the decrease in IP is as much as expected. Thereafter, the decrease in IP is low.

Reason:

Poor screening effect of d e^- in As, Sb & d, f e^- in Bi

• Due to its small size, N has abnormally higher IP.

• IP of $IV_A < V_A < VI_A$ $\quad (IV_A < V_A > VI_A)$

Ex:1. IP of C < O < N $\quad$ C < N > O

2. IP of Si < P > S

Reason: 5th group elements have half filled p-subshell.

6. Electronegativity (On Pauling's scale)

N	P	As	Sb	Bi
3.0	2.1	2.0	1.9	1.9

7. Electronaffinity : P $\xrightarrow{\text{dec}}$ Bi

EA of N < P (Due to small size, more repulsions among e^- in N)

Reason:

Due to the small size of N, there exist greater inter electronic repulsions between the e^- already existing and the added e^-.

Similarly EA of F < Cl

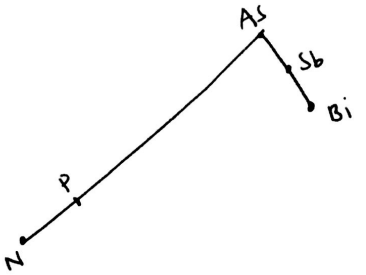
O < S

***

• N has higher positive electron gain enthalpy.

so its EA is taken as 0.

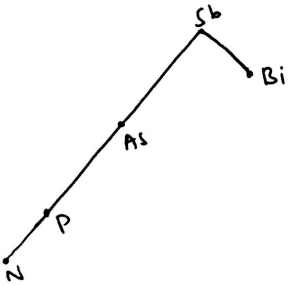
8. MP



- N is a gas.
- P is a waxy solid.
- In As, 5 e^- are available for forming 5 covalent bonds so metallic bond strength is maximum
- In Sb, Bi, due to inert pair effect, only 3 e^- are available for forming 3 covalent bonds. So the metallic bonds are weaker in Sb & Bi.

  ∴ MP of Sb, Bi < As

9. BP



BP of Nitrogen = −195.8°C

- Catenation:

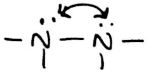
C > Si > S > P > N > As > Sb

Reason: catenation power)

Bond energy of C-C > Si-Si > S-S > P-P > N-N > As-As > Sb-Sb

- Bond energy of N-N < P-P

Reason - Due to the small size of N, N-N bond length is shorter. So there exist greater repulsions among the lone pairs on N atoms. These repulsions weaken the bond between N atoms.



- Nitrogen forms N_3^- (azide) due to catenation

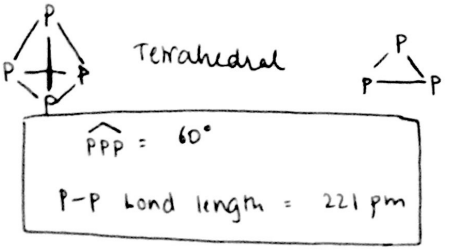
II. Atomicity

- Nitrogen is diatomic (N_2) $:N \equiv N:$ BO = 3
- Nitrogen is chemically inert on account of its high BDE 945.4 KJ/mol.
- CO, NO^+, CN^- are isoelectronic with N_2 and have bond order 3.
- CO, NO^+, CN^- are more reactive than N_2.

  Reason:

  CO, NO^+, CN^- are polar while N_2 is non-polar.
- Among homodiatomic molecules, N_2 has highest bond energy.

- P, As, Sb are tetraatomic molecules (P_4, As_4, Sb_4)



6 - covalent bonds

$\Delta H_{diss} = 6 \times E_{P-P}$

Due to high bond angle strain, P_4 molecule is highly reactive.

- Bi is mono atomic.

12. Multiple Bond formation

a) Nitrogen forms effective $p\pi-p\pi$ bonds.

Reason:

Small size and high EN.

b) P, As, Sb, Bi cannot form effective $p\pi-p\pi$ bonds.

Reason:

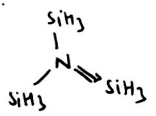
Due to large size, the p-orbitals are more dispersed which results in ineffective overlapping.

c) N cannot form $p\pi-d\pi$ bonds.

Reason:

N has no vacant d-orbitals

Exceptions:



d) P, As, Sb, Bi can readily form $p\pi-d\pi$ bonds.

Reason:

Availability of d-orbitals

e) P, As, Sb, Bi form $d\pi-d\pi$ bonds with metals while acting as ligands.

Ex: $X_3P \leftarrow O$ $R_3P=CH_2$ $R_3P=O$ $Ph_3P=O$ } Contain $p\pi-d\pi$ bonds

Ex: PPh_3, $As(C_2H_5)_3$

- Dipole moment of $R_3NO > R_3PO$ even though N-O is less polar than P-O.

Reason:

Due to back bonding R_3PO, its dipole moment is low.

Back bonding ligands (Non classical / π-accepting ligands)

PF_3, PR_3, PPh_3, PH_3, CN^-, NO^+

13. Oxidation States

- Common O.S = $-3, +3, +5$

- The tendency to exhibit -3 decreases down the group.

Reason:

EN decreases and metallic nature increases.

- Stability of $+3$ state increases while $+5$ state decreases down the group.

Reason:

on moving down the group, inert pair effect increases.

- Bi cannot form pentahalides except $\boxed{BiF_5}$

Reason: Prominent inert pair effect.

- Bi cannot form Bi_2O_5.

Reason: Inert pair effect.

- N cannot form pentahalides and doesn't form N^{+5} isolated ion.

Reason:

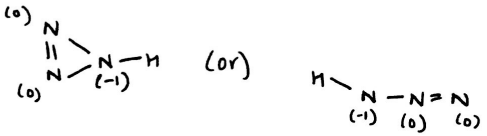
Absence of d-orbitals.

- N exhibits a wide range of oxidation states from −3 to +5

Nitrogen:

NH_3 (−3)
N_2H_4 (−2)
NH_2OH (−1)
N_2 (0)
N_2O (+1)
NO (+2)
N_2O_3 (+3)
HNO_2 (+3)
NO_2 (+4)
N_2O_5 (+5)
HNO_3 (+5)

N exhibits a fractional O.S $-1/3$ in its acidic hydride N_3H (hydrazoic acid)



Hydrazoic acid (N_3H)

Individual O.S = 0, 0, −1

Avg = $-1/3$

- The OS of Nitrogen from +1 to +4 undergo DPP in both acidic & alkali soln.

- $\underset{(+3)}{3HNO_2} \longrightarrow \underset{(+5)}{HNO_3} + \underset{(+2)}{NO} + H_2O$

- $\underset{(+4)}{2NO_2} + 2NaOH \longrightarrow \underset{(+3)}{NaNO_2} + \underset{(+5)}{NaNO_3} + H_2O$

Comproportionation rxns

$\underset{(-3)\ (+5)}{NH_4NO_3} \longrightarrow \underset{(+1)}{N_2O} + 2H_2O$

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(-3) (+3) (0)

* All intermediate OS of Phosphorus undergo DPP in acidic / alkaline med

- $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

  (0) (-3) (+1)

- $2H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3$

  (+1) (+5) (-3)

- SbF_3 & BiF_3 are ionic

- Sb^{+3}, Bi^{+3} ions are unstable in aq. soln.

They readily undergo hydrolysis forming oxy chlorides

$$Sb^{+3} + H_2O \rightleftharpoons SbO^+ + 2H^+$$

$$Bi^{+3} + H_2O \rightleftharpoons BiO^+ + 2H^+$$

- Sb^{+3}, Bi^{+3} are stable only in presence of strong acidic med.
  (Conc. of H^+ increases so eq. shifts backward)

- As^{+3}, Sb^{+3}, Bi^{+3} are stable towards DPP, i.e. do not undergo DPP.

  Reason: Inert pair effect

Covalency

- Max covalency of N is 4.
- N cannot extend its covalency beyond 4 due to absence of d-orbitals

$$NH_3 + H^+ \longrightarrow NH_4^+ \qquad NR_3 + R^+ \longrightarrow NR_4^+$$

- P, As, Sb, Bi can extend their covalency beyond 4 due to * vacant d-orbitals

$2SbF_5 + F^- \longrightarrow Sb_2F_{11}^-$

15: Allotropy

a) Allotropes of N

- N has no allotropes in gaseous state but has two allotropes in solid state.

α- Nitrogen (cubic crystalline)

β- Nitrogen (hexagonal crystalline)

b) Allotropes of P

- White/yellow
- Red
- Scarlet
- Black

i) White phosphorus

- Translucent white waxy solid.
- Consists of discreet P_4 units.
- Due to high bond angle strain, it is highly reactive

- Ignites even at 35°C, so it is stored under water.
- Burns in moist air spontaneously giving bright light. This phenomenon is called 'chemiluminiscence'

- Insoluble in water but soluble in CS_2.
- Above 800°C, it decomposes to P_2 units, which contain very weak $p\pi$-$p\pi$ bonds

$$P_4 \xrightarrow{> 800^\circ C} 2P_2$$

$$P \equiv P \quad (BE = 489.3\ kJ/mol)$$

- White phosphorus vapours are toxic which causes phossy jaw disease (degradation of jaw bones)
- This is the standard state of phosphorus.

ii) Red phosphorus

- Red crystalline solid
- Polymer of P_4 units.

White P $\xrightarrow[\text{Inert atmosphere}]{250-300^\circ C}$ Red-P

White P $\xrightarrow[\text{sunlight}]{\text{low T}}$ Red-P

- Less reactive
- Need not be stored under water
- Doesn't ignite until 400°C
- It's vapours are non-toxic
- Insoluble in both water & CS_2.

iii) Black phosphorus

1. α- Black

- Red-P $\xrightarrow[\text{Sealed tube}]{520^\circ C}$ α- Black

- Exists in orthorhombic, rhombohedral & monoclinic forms.
- Doesn't burn in air.
- Undergoes sublimation

2. β-black:

- White-P $\xrightarrow[200°C]{\text{high pressure}}$ β-black

*. Thermodynamically most stable allotrope of P

- Contains layer structure of hexagonal rings of P atoms (P atoms in chair form)
- Doesn't catch fire until 400°C

c) Allotropes of As

- Grey
- Yellow
- Black

d) Allotropes of Sb

- Yellow
- Metallic
- Explosive

***

e) Bi doesn't exhibit allotropy.

1. Occurence

- Relative abundance in Earth's crust : P > N > As > Sb > Bi

- N is available as:
  - Chile Salt petre → $NaNO_3$
  - Indian salt petre → KNO_3
  - Air has 78% by volume N_2

- P is available as:

  Phosphorite $3Ca_3(PO_4)_2$

  Fluoroapatite $3Ca_3(PO_4)_2 \cdot CaF_2$

  Chloro apatite $3Ca_3(PO_4)_2 \cdot CaCl_2$

  Hydroxy apatite $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$

  Bone ash contains 80% P

- As is available as $CoAsS$ - cobaltite

- Sb is available as

  Sb_2S_3 → Stibinite

  Sb_2O_3 → Flue dust

- Bi is available as

  Bi_2S_3 → Bismuthite

  Bi_2O_3 → Bismuth ochre

1. Hydrides of 15th group

MH_3 type :	NH_3	PH_3	AsH_3	SbH_3	BiH_3
(covalent)	Ammonia	Phosphine	Arsine	Stibine	Bismuthine

• Prep. methods

1. • $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

(Any ionic nitride)

• $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

2. • $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

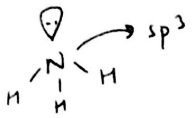
3. $Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3$ (Also by treating with H_2O)

4. $Zn_3Sb_2 + 6HCl \longrightarrow 3ZnCl_2 + 2SbH_3$ (Also by treating with H_2O)

5. $2Na_3Bi + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2BiH_3$

• Structural aspects

Pyramidal with 1 lp on central atom



Due to lp-bp repulsions, bond angle is 107°

Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Bond angle	107°	93°	91°	91°	90°

NH_3: sp^3 hbd

lp-bp repulsions

PH_3, AsH_3, SbH_3, BiH_3: pure-p (Angle between any 2 p-orbitals = 90°)

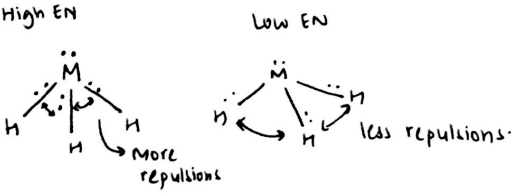
lone pair in pure-s orbital.

- In NH_3, N is in sp^3 hybridised state.

  Due to lp-bp repulsions, bond angle decreases to 107°.

- In other hydrides, bond angles are close to 90° due to involvement of pure p-orbitals in bonding while the lone pair resides in s-orbital.

*. Bond angle decreases from NH_3 to BiH_3.



Reason: Decrease in EN of central atom.

- Properties of hydrides:

  - Colourless, poisonous gases
  - Covalent nature : NH_3 —Inc→ BiH_3

    Ionic nature : NH_3 —Dec→ BiH_3

- Thermal stability : $NH_3 \xrightarrow{Dec} BiH_3$

Reason:

M-H	Bond energy
N–H	↓ Dec
P–H	
As–H	
Sb–H	
Bi–H	

As size of central atom decreases, extent of overlapping decreases

∴ stability decreases.

- M-H bond energy decreases. (As size of central atom ↑, extent of overlap ↓, bond energy ↓)

*

- BiH_3 decomposes even at room temp.

- Ease of formation : $NH_3 \xrightarrow{Dec} BiH_3$ (∵ Thermal stability of NH_3 is more & ΔH_f for NH_3 is more -ve)

- Ease of replacement of H with Cl or CH_3 : $NH_3 \xrightarrow{Dec} BiH_3$

(since overlapping decreases when smaller Hs are replaced by larger halogen/methyl groups and bond energy decreases)

∴ Thermal stability ↓

- Reducing nature/power:

$NH_3 \xrightarrow{Inc} BiH_3$

Reason: M-H bond energy decreases.

- NH_3 generally doesn't act as reductant whereas the other hydrides are good reductants. (In some cases, NH_3 acts. Refer ammonia)

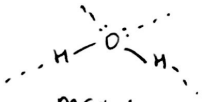
- Hydrogen bond forming tendency:

$NH_3 \xrightarrow{Dec} BiH_3$

Reason: Polarity of M-H bond decreases.

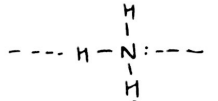
- H-bonding is seen only in NH_3.

- NH_3 has H-bonding in solid & liquid states but not in vapour phase.



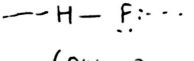
max 4 H-bonds

2 lp, 2 H



(Only 2 max no. of H-bonds)

1 lp, 1 H participates in H-bonding



(Only 2 max H-bonds)

Only 1 lp, 1 H participate in H bonding)

Molecule	H_2O	NH_3	HF
Max. no. of H bonds formed	4	2	2

- Solubility in water:

$NH_3 \xrightarrow{decreases} BiH_3$

Reason: H-bond forming tendency with H_2O molecules decreases.

- NH_3 solvent undergoes self dissociation & auto protolysis.

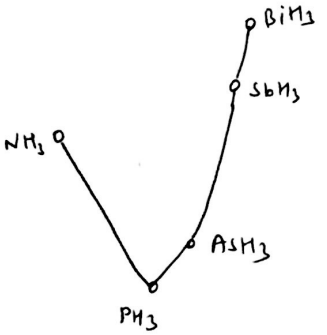
$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$K_d = [NH_4^+][NH_2^-] = [NH_4^+]^2 = [NH_2^-]^2$$

- Alkali and alkoline earth metals in NH_3 produce deep blue solns. due to formation of ammoniated e^-.

These solutions act as mixed conductors & powerful reductants.

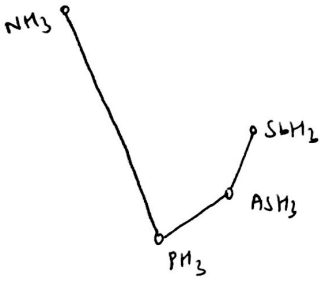
- **B.P:**



All are gases at room temp.

The abnormally higher B.P of NH_3 is due to intermolecular H-bonding

- **M.P:**



Abnormally higher BP & MP of NH_3 is due to H-bonding

- **Volatility:** $\boxed{\text{Volatility} \propto \frac{1}{\text{BP}}}$

Volatility : $PH_3 > AsH_3 > NH_3 > SbH_3 > BiH_3$ (NH_3 is less volatile due to H-bonding)

Lewis - basic nature:

$NH_3 \xrightarrow{\text{Dec}} BiH_3$

Reason: As size of central atom increases, the lone pair gets dispersed in larger and larger volumes. So, the lp density decreases.

∴ Lone pair becomes less available for donation.

(In PH_3, AsH_3, SbH_3, BiH_3 lp is present in more EN s-orbital)

- Basic nature of $NH_3 < N(CH_3)_3$

  $NH_3 > NCl_3$

  $PH_3 < P(CH_3)_3$

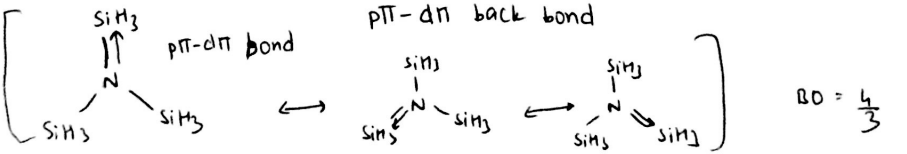
- Basic nature of $NH_3 > N(SiH_3)_3$ (back bonding)

  $NH_3 > N(GeH_3)_3$

Reason: In $N(SiH_3)_3$ & $N(GeH_3)_3$, the lp on N is utilized for forming back bonding.

- NH_3, $N(CH_3)_3$ → sp^3 hbd
  Pyramidal
  No back bonding

- $N(SiH_3)_3$, $N(GeH_3)_3$ → sp^2 hbd
  planar triangle
  $p\pi - d\pi$ back bond



- $P(CH_3)_3$, $P(SiH_3)_3$, $P(GeH_3)_3$ → P in sp^3 hbd

  Pyramidal

  No back bonding due to large size of P

- Basic strength of $NH_3 > N_2H_4 > NH_2OH$ (-I effect for lp)

Complex forming tendency

$$NH_3 \xrightarrow{dec} BiH_3$$

Reason: In NH_3, lp is in sp^3 hbd orbital whereas in other hydrides it is in s-orbital. On moving down, the nuclear charge increases which holds the s-electron pair tightly. So the s-e^- pair shows reluctance towards bonding.

∴ Complex forming tendency decreases.

2. Oxides

M_2O_3	M_2O_5	Basic nature	Stability	Acidic nature
N_2O_3	N_2O_5			
$P_2O_3 \rightleftharpoons P_4O_6$	$P_2O_5 \rightleftharpoons P_4O_{10}$	Inc ↓	Dec (LE) ↓	Dec ↓
$As_2O_3 \rightleftharpoons As_4O_6$	$As_2O_5 \rightleftharpoons As_4O_{10}$			
$Sb_2O_3 \rightleftharpoons Sb_4O_6$	$Sb_2O_5 \rightleftharpoons Sb_4O_{10}$			
Bi_2O_3	–			

Stability → Inc

Acidic nature → Inc

Basic nature → Dec

- Bi_2O_3 is ionic.
- Bi doesn't form Bi_2O_5 due to inert pair effect
- Most acidic oxide – N_2O_5

  Most basic oxide – Bi_2O_3

  Amphoteric oxides – As_2O_3 & Sb_2O_3
- As_2O_5 & Sb_2O_5 are good oxidants.
- As_2O_5 dissolves in water producing H_3AsO_4
- Sb_2O_5 is insoluble in water
- As_2O_3 dissolves (sparingly soluble) in H_2O while Sb_2O_3 is insoluble.

a) Oxides of Nitrogen

Nitrogen oxides: N_2O (+1), NO (+2), N_2O_3 (+3), $NO_2 \rightleftharpoons N_2O_4$ (+4), N_2O_5 (+5)

Acidic nature → Inc

2. Oxides

M_2O_3	M_2O_5
N_2O_3	N_2O_5
$P_2O_3 \rightleftharpoons P_4O_6$	$P_2O_5 \rightleftharpoons P_4O_{10}$
$As_2O_3 \rightleftharpoons As_4O_6$	$As_2O_5 \rightleftharpoons As_4O_{10}$
$Sb_2O_3 \rightleftharpoons Sb_4O_6$	$Sb_2O_5 \rightleftharpoons Sb_4O_{10}$
Bi_2O_3	–

Basic nature: Inc ↓

Stability: Dec (LE) ↓

Acidic nature: Dec ↓

Stability: Inc →

Acidic nature: Inc →

Basic nature: Dec →

- Bi_2O_3 is ionic.
- Bi doesn't form Bi_2O_5 due to inert pair effect
- Most acidic oxide – N_2O_5

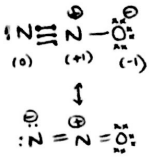
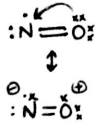
  Most basic oxide – Bi_2O_3

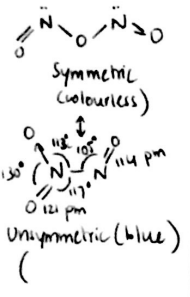
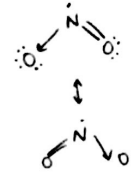
  Amphoteric oxides – As_2O_3 & Sb_2O_3
- As_2O_5 & Sb_2O_5 are good oxidants.
- As_2O_5 dissolves in water producing H_3AsO_4
- Sb_2O_5 is insoluble in water
- As_2O_3 dissolves (sparingly soluble) in H_2O while Sb_2O_3 is insoluble.

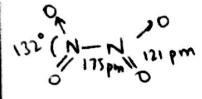
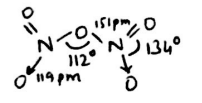
a) Oxides of Nitrogen

Nitrogen oxides: N_2O (+1), NO (+2), N_2O_3 (+3), $NO_2 \rightleftharpoons N_2O_4$ (+4), N_2O_5 (+5)

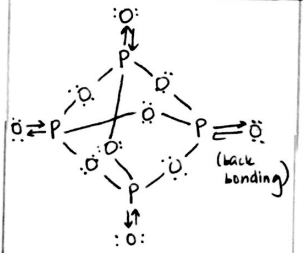
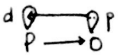
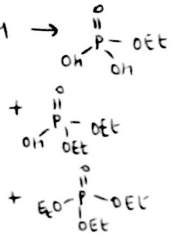
Acidic nature: Inc →

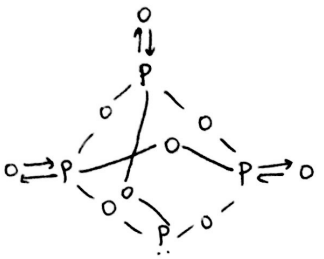
Oxide of N	Formula	Prep.	Chemical properties	Important aspects
Nitrous oxide 	N_2O	• $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ • $Zn + HNO_3 \text{ (dil)} \longrightarrow Zn(NO_3)_2 + N_2O + H_2O$ • ~~$2NO + H_2S \longrightarrow N_2O + H_2O + S$~~ • $HNO_3 + SnCl_2 + HCl \longrightarrow N_2O$	• $NaNH_2 + N_2O \longrightarrow NaN_3 + NH_3 + NaOH$ • $N_2O + Cu \xrightarrow{CuO} CuO + N_2$ • $N_2O + Mg \longrightarrow N_2 + MgO$ • $N_2O + 2Na \longrightarrow N_2 + Na_2O$	• Colourless gas • Neutral to litmus • Laughing gas • Used as anaesthesia • Insoluble in H_2O
Nitric oxide 	NO	• $FeSO_4 + NaNO_2 + H_2SO_4 \text{ (dil)} \longrightarrow Fe_2(SO_4)_3 + NO + Na_2SO_4 + H_2O$ • $Cu + HNO_3 \text{ (dil)} \longrightarrow Cu(NO_3)_2 + NO + H_2O$ • $HNO_2 + 2I^- + H^+ \longrightarrow I_2 + NO + H_2O$ • $NO_2 + H_2S \longrightarrow NO + S + H_2O$ • $NO_2 + SnCl_2 + HCl \longrightarrow NO$	• $FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$ (Brown ring) • $2NO + Cl_2 \longrightarrow 2NOCl$ • $2NO + O_2 \longrightarrow 2NO_2$ • $4NO + [Cr(CO)_6] \longrightarrow [Cr(NO)_4] + 6CO$ ($3e^-$ donor) • $NO + [Fe(CO)_5] \longrightarrow [Fe(CO)_2(NO)_2] + 3CO$ • Decolourizes acidified $KMnO_4$ $NO + KMnO_4 + H_2SO_4 \longrightarrow HNO_3 + H_2O + MnSO_4 + K_2SO_4$ • ~~$2NO + 2HNO_3 \longrightarrow 3NO + H_2O$~~	• Colourless gas • Neutral towards litmus • Odd e^- molecule • Paramagnetic • 3 e^- donor • Acts as bridged ligand • Ambident ligand • In solid & liquid states, it exists as dimer N_2O_2 which is diamagnetic • Its MOC is similar to O_2 • Insoluble in H_2O

Nitrogen sesqui oxide  Symmetric (colourless) Unsymmetric (blue)	N_2O_3	• $2NO + N_2O_4 \xrightarrow[\text{cooled}]{250\,K} 2N_2O_3$	• $N_2O_3 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$ • $N_2O_3 + 2HClO_4 \longrightarrow 2NOClO_4 + H_2O$ • $N_2O_3 + H_2O \longrightarrow 2HNO_2$ • $N_2O_3 + NaOH \longrightarrow 2NaNO_2 + H_2O$	• Dark blue in liq. state & pale blue in solid state • Blue solid/liquid • Acidic oxide • In solid state, it contains NO^+ & NO_2^- ions. • Dissolves in H_2O
Nitrogen dioxide  134° 120 pm		• $Pb(NO_3)_2 \longrightarrow PbO + NO_2 + O_2$ • $Cu + HNO_3\ (conc) \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$	• $NO_2 + F_2 \longrightarrow NO_2F_2$ • $NO_2 + CO \longrightarrow NO + CO_2$ • $NO_2 + H_2S \longrightarrow NO + H_2O + S$ • $2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$ • $NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$	• Reddish brown gas • Dissolves in H_2O • Acidic oxide • Harmful & causes respiratory disorders. • odd e^- molecule • Paramagnetic

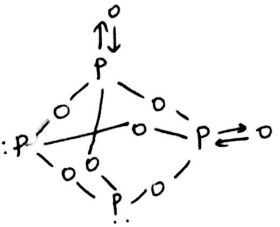
Oxide of N	Formula	Prep.	Chem. properties	Imp. aspects
Dinitrogen tetroxide  (Dimer of NO_2)	N_2O_4	$2NO_2 \xrightarrow[\text{cooled}]{-1^\circ C} N_2O_4$	• $2N_2O_4 + ZnCl_2 \rightarrow Zn(NO_3)_2 + 2NOCl$ • $2N_2O_4 + TiI_4 \rightarrow Ti(NO_3)_2 + 2NO + 2I_2$ • $N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$ (Dissolves in H_2O giving same acids) • $N_2O_4 + NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$	• Colourless liquid/solid • In liquid state serves as non-aqueous solvent due to presence of NO^+ & NO_3^- ions. • Acidic oxide $N_2O_4 \rightarrow \underset{\text{(Acid)}}{NO^+} + \underset{\text{(Base)}}{NO_3^-}$ • $NOCl + NaNO_3 \rightarrow NaCl + N_2O_4$ (Acid, Base, salt, solvent) • Diamagnetic • Undergoes complete diss. at 140°
Dinitrogen pentoxide 	N_2O_5	$2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$	• $N_2O_5 + H_2O \rightarrow 2HNO_3$ • $N_2O_5 + 2NaOH \rightarrow 2NaNO_3$ • $N_2O_5 + Na \rightarrow NaNO_3 + NO_2$ • $N_2O_5 + NaCl \rightarrow NaNO_3 + NO_2Cl$ • $N_2O_5 \xrightarrow{\Delta} NO_2 + NO + O_2$	• Dissolves in H_2O • Colourless, ionic solid oxide • Acidic in nature • Called 'nitronium nitrate' since it contains NO_2^+ & NO_3^- • Sublimes at 305 K

b) Oxides of Phosphorus

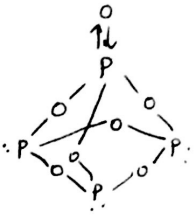
Oxide	Prep.	Structure	Imp. aspects
Phosphorus trioxide (P_4O_6)	$P_4 + 3O_2 \longrightarrow P_4O_6$ (limited)	• P atoms in tetrahedral arrangement joined by oxygen bridges • 6 oxygen bridges • 16 lp	• Acidic oxide • Acts as lewis acid • Dissolves in water $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$ • P_4O_6 when heated in vaccuum produces red P and other higher oxides $P_4O_6 \xrightarrow[\text{vaccuum}]{\Delta} P\ (\text{Red}) + P_4O_7 + P_4O_8 + P_4O_9 + P_4O_{10}$ • Soft, white, waxy solid
Phosphorus pentoxide (P_4O_{10})	$P_4 + 5O_2 \longrightarrow P_4O_{10}$ (excess)	 • P atoms are tetrahedrally arranged and are joined by oxygen bridges. • No. of oxygen atoms around each P = 4 • Total 20 lp • Contains 4 $p\pi - d\pi$ back bonds 	• Acidic oxide & lewis acid • High affinity for water and hence acts as dehydrating agent. • Dissolves in water $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ • White crystalline solid. • P_4O_{10} forms Phosphoesters with alcohols and ethers. $P_4O_{10} + EtOH \rightarrow$  • $P_4O_{10} + Et_2O \rightarrow O=P(OEt)_3$



P_4O_9 (remove one oxygen)



P_4O_8



P_4O_7

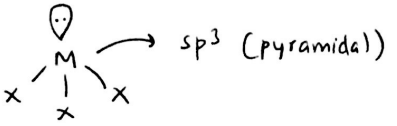
- $P_4O_{10} + 10C \longrightarrow 4P + 10CO$
  (coke) (Red)

  $P_4O_{10} + CaO \longrightarrow Ca_3(PO_4)_2$

- Both P_4O_6 & P_4O_{10} have garlic smell.

3. Halides

a) Trihalides: (MX_3)



sp^3 (pyramidal)

- NF_3 is stable while NCl_3, NBr_3, NI_3 are unstable.
- NCl_3 is highly explosive
- NBr_3 & NI_3 form unstable ammoniates which detonate on heating.

$NBr_3 \cdot 6NH_3$ & $NI_3 \cdot 6NH_3$

$$8NI_3 \cdot NH_3 \xrightarrow{\Delta} 5N_2 + 9I_2 + 6NH_4I$$
(s) (g) (g) (g)

Due to the production of huge volume of gases, it detonates explosively.

- NF_3 and PF_3 are resistant to hydrolysis.

Reason: i) • In NF_3, neither N nor F have d-orbitals. So they cannot accept e^- pairs from H_2O

• NF_3 undergoes hydrolysis under drastic conditions by SN^1 mech.

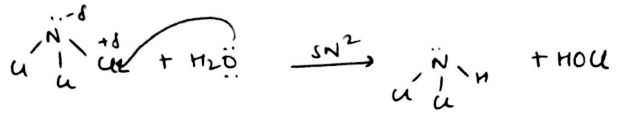
$$NF_3 \rightleftharpoons NF_2^{\oplus} + F^-$$

$$H_2O + NF_2^{\oplus} \longrightarrow H_2O{\to}NF_2$$

ii) In PF_3, even though P has vacant d-orbitals, due to back bonding from F, it cannot accept e^- pair from H_2O.

- Hydrolysis of trichlorides:

1. $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$ (SN^2 mech)
(-3) (base) (acid)

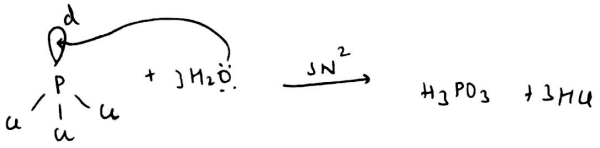


- O.S of N in NCl_3 is -3
- $HOCl \longrightarrow HCl + (O)$ (unstable)

$\therefore$ Aq. soln. of NCl_3 acts as oxidant and bleaching agent due to the production of nascent oxygen.

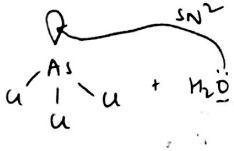
2. $PCl_3 + 3H_2O \longrightarrow \underset{(B=2)}{H_3PO_3} + \underset{(B=1)}{3HCl}$

Aq. soln. of PCl_3 acts as good conductor due to formation of strong electrolyte HCl.



O.S of P in $PCl_3 = +3$

3. $AsCl_3 + 3H_2O \longrightarrow \underset{(B=2)}{H_3AsO_3} + \underset{(B=1)}{3HCl}$



O.S of As is $AsCl_3 = +3$

1. $SbCl_3 + H_2O \rightleftharpoons \underset{\text{(white turbidity)}}{SbOCl\downarrow} + 2HCl$ — partial hydrolysis

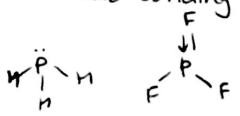
5. $BiCl_3 + H_2O \rightleftharpoons BiOCl\downarrow + 2HCl$ Partial hydrolysis

(white turbidity)

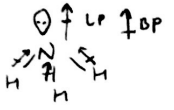
Pearl of white

- Extent of hydrolysis : $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$
- Basic strength of $NF_3 < NCl_3 < NBr_3 < NI_3$
- Bond angle in $PH_3 < PF_3$ (back bonding)

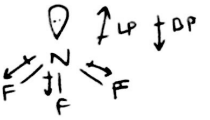
PH_3 has no back bonding while PF_3 has back bonding



- Dipole moment of $NF_3 < NH_3$



$\mu = \mu_{LP} + \mu_{BP}$



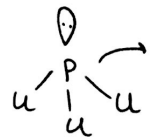
$\mu = \mu_{LP} \sim \mu_{BP}$

- BiF_3 - ionic

SbF_3 - Ionic > covalent

Phosphorus trihalides

PCl_3



sp^3 (pyramidal)

Colourless oily liquid.

Colourless

- ~~Yellow~~ oily liquid

Prep:

$$P_4 + Cl_2 \text{ (limited)} \longrightarrow 4PCl_3$$

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 2S_2Cl_2 + 4SO_2$$

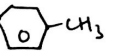
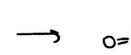
Chem. properties

- $PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$
- $PCl_3 + Cl_2 \xrightarrow{CCl_4} PCl_5$
- $PCl_3 + S \longrightarrow PSCl_3$
- $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$
- $PCl_3 + SOCl_2 \longrightarrow PSCl_3 + POCl_3 + PCl_5$
- $PCl_3 + 3C_2H_5OH \longrightarrow 3C_2H_5Cl + H_3PO_3$
- $PCl_3 + S_2Cl_2 \longrightarrow PSCl_3 + PCl_5$
- $PCl_3 + 3CH_3COOH \longrightarrow 3CH_3COCl + H_3PO_3$
- $PCl_3 + 6NH_3 \longrightarrow P(NH_2)_3 + 3NH_4Cl$
- $2PCl_3 + 6Cl_2 + P_4O_6 \longrightarrow 6POCl_3$
- $PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$

$POCl_3$

- $POCl_3$ forms phosphoesters with ~~ethyl~~ alcohols ~~and ethers.~~

- $O{=}PCl_3 + 3C_2H_5OH \longrightarrow O{=}P(OEt)(OEt)(OEt)$

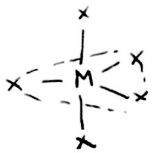
- $O{=}PCl_3 + 3$  $\longrightarrow O{=}P(O$  $)_3 + 3HCl$

- $PCl_3 + \frac{1}{2}O_2 \xrightarrow{\Delta} POCl_3$

- PF_3 & PCl_3 can ~~form~~ coordinate with haemoglobin. So they too retard oxygen transportation.
- PF_3 involves in back bonding like CO

$$[Ni(CO)_4] + 4PF_3 \longrightarrow [Ni(PF_3)_4] + 4CO$$

b) Pentahalides (MX_5)



sp^3d hbd (sp^2+pd) TBP

By bent rule : axial → More EN atoms

equitorial → less EN atom

- N cannot form pentahalides

  Reason: Absence of d-orbitals

- Bi cannot form pentahalides except BiF_5

  Reason: Inert pair effect

- BiF_5 is a good fluorinating agent

  $UF_4 \longrightarrow UF_6$

  $BrF_3 \longrightarrow BrF_5$

  $H_2O \longrightarrow O_3 + OF_2$

- PF_5 - covalent colourless gas

  $5AsF_3 + 3PCl_5 \longrightarrow 3PF_5 + 5AsCl_3$

- PCl_5 - yellowish white ionic solid (PCl_4^+, PCl_6^-)

- PCl_4^+ (sp^3 - tetrahedral)

  PCl_6^- (sp^3d^2 - octahedral)

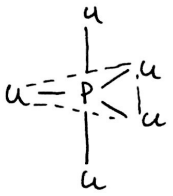
- PBr_5 - ionic solid (PBr_4^+, Br^-)

- PI_5 - ionic solid (PI_4^+, I^-)

  PI_5 hardly exists because of steric crowding of bulkier iodines.

- $As_2O_3 + 5F_2 \longrightarrow 2AsF_5 + \frac{3}{2}O_2$
- $Sb_2O_3 + 5F_2 \longrightarrow 2SbF_4 + \frac{3}{2}O_2$

Phosphorus pentachloride (PCl_5)



P–Cl (axial) 240 pm

P–Cl (equitorial) 202 pm

sp^3d hbd

In gaseous, liquid states

In solid → ionic

- In P, the size of 3d orbitals is very much greater than 3s & 3p.

On approach of strong EWG such as Cl^-, the 3d orbitals contraction occurs so that the size of 3d orbitals becomes nearly equal to 3s & 3p. Then, they involve in sp^3d hybridization.

Prep:

1. $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$
2. $P_4 + 10Cl_2 \longrightarrow 4PCl_5$ (excess)
3. $PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$

- $PCl_3 + 3HOH \longrightarrow H_3PO_3 + 3HCl$
- $3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3$
- $PCl_3 + Ag \xrightarrow{\text{(metals)}} P_4 + AgCl$

  $PCl_3 + Na \longrightarrow NaCl + Na_3P$
- $PCl_3 + S_2Cl_2 \longrightarrow PCl_5 + PSCl_3$

  $PCl_3 + SOCl_2 \longrightarrow PCl_5 + POCl_3 + PSCl$
- $PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$

  $PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$
- $PCl_3 + O_2 \longrightarrow POCl_3$

  $PCl_3 + S \longrightarrow PSCl_3$
- $PCl_5 + Cu \longrightarrow CuCl + PCl_3$

  $PCl_5 + Sn \longrightarrow SnCl_4 + 2PCl_3$

Chemical properties

- $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ (partial hydrolysis)

  $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$

$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$ (complete hydrolysis)

* $AsCl_5$ also undergoes hydrolysis in the same way.

- $PCl_5 + H_2SO_4 \longrightarrow Cl-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Cl + POCl_3 + H_2O$

2. $PCl_5 + C_2H_5OH \longrightarrow POCl_3 + C_2H_5Cl + HCl$

$POCl_3 + 3C_2H_5OH \longrightarrow H_3PO_4 + 3C_2H_5Cl$

$PCl_5 + 4C_2H_5OH \longrightarrow H_3PO_4 + 4C_2H_5Cl + HCl$

3. $PCl_5 + CH_3COOH \longrightarrow POCl_3 + CH_3COCl + HCl$

$POCl_3 + 3CH_3COOH \longrightarrow H_3PO_4 + 3CH_3COCl$

$PCl_5 + 4CH_3COOH \longrightarrow H_3PO_4 + 4CH_3COCl + HCl$

4. $PCl_5 + 2Ag \longrightarrow 2AgCl + PCl_3$

$2PCl_5 + Sn \longrightarrow SnCl_4 + 2PCl_3$

5. $6PCl_5 + P_4O_{10} \longrightarrow 10\,POCl_3$

6. $PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$

7. $n\,PCl_5 + n\,NH_4Cl \longrightarrow \underset{\text{Cyclic rings } (n=3\text{-}8)}{(NPCl_2)_n} + \underset{\text{linear polymer}}{PCl_4(NPCl_2)_n NPCl_3} + HCl$

Rxns: phosphonitrilic polymer

- $PCl_5 + C_2H_5OH \longrightarrow C_2H_5Cl + POCl_3 + HCl$

  $PCl_5 + CH_3COOH \longrightarrow CH_3COCl + POCl_3 + HCl$

- $PCl_5 + SO_2(OH)_2 \xrightarrow{(H_2SO_4)} SO_2Cl_2 + POCl_3 + HCl$

- $PCl_5 + P_2N(OH)_3$

Oxo acids

- ous acids (H_3MO_3)
- ic acids (H_3MO_4)

- Acidic strength of $H_3MO_3 < H_3MO_4$

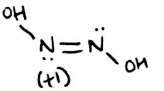
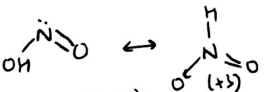
  Acidic strength of $H_3PO_3 > H_2AsO_3 > H_3SbO_3$

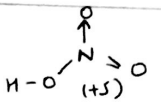
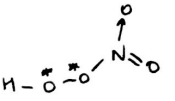
  $H_3PO_4 > H_3AsO_4 > H_3SbO_4$

- $M_2O_3 + 3H_2O \longrightarrow 2H_3MO_3$

  $M_2O_5 + 3H_2O \longrightarrow 2H_3MO_4$

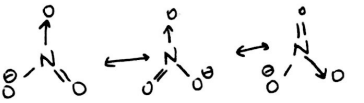
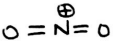
1. Oxo acids of Nitrogen

Oxo acid	Formula	Structure	Imp. aspects
Hypo nitrous acid	$H_2N_2O_2$ $N \rightarrow +1$ Emp = HNO	 N-sp^2	• Dibasic acid • Forms two series of salts (acidic & normal)
Nitrous acid	HNO_2 $N \rightarrow +3$	 N-sp^2 Tautomeric forms	• Monobasic acid • Acts as both oxidant & reductant • It oxidises: $Sn^{+2} \longrightarrow Sn^{+4}$ $Fe^{+2} \rightarrow Fe^{+3}$ $I^- \longrightarrow I_2$ $S \longrightarrow SO_2$ $H_2S \rightarrow S$ $AsO_3^{2-} \longrightarrow AsO_4^{2-}$ While it acts as oxidising ag it gets reduced to NO $HNO_2 \longrightarrow NO$

Oxo acid	Formula	Structure	Imp. aspects
			• It reduces: $MnO_4^- \rightarrow Mn^{+2}$ $Cr_2O_7^{2-} \rightarrow Cr^{+3}$ $H_2O_2 \rightarrow H_2O$ $Br_2 + H_2O \rightarrow HBr$ While it acts as RA, it is oxidised to HNO_3 $HNO_2 \longrightarrow HNO_3$ • $3HNO_2 \rightarrow HNO_2 + 2NO + H_2O$
Nitric acid (Aqua fortis)	HNO_3 $N \rightarrow +5$		• Monobasic acid • Good oxidant
Per nitric acid	HNO_4 $N \rightarrow +5$		• Monobasic acid • Powerful oxidant

Acid	Anhydride	
HNO_2	N_2O_3	
$HNO_2 + HNO_3$	$N_2O_4 \rightleftharpoons 2NO_2$	(Mixed anhydride)
HNO_3	N_2O_5	

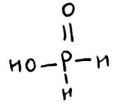
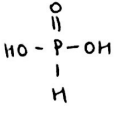
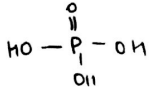
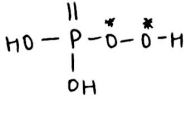
• N_2O is incoluble in water. So it is not regardeds as anhydride of $H_2N_2O_2$ (Since anhydrides are cuppoxed to hydrolyse and give the original compound back)

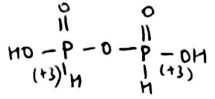
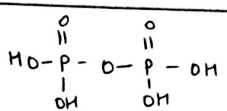
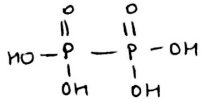
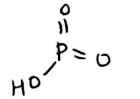
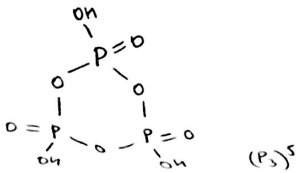
Ion	Hbd	Structure	Bond order
Nitrite ion (NO_2^-)	(sp^2 + 1 Lp) Angular		BO = $\frac{1+2}{2}$ = 1.5
Nitrate ion (NO_3^-)	(sp^2) + 0 lp triangular planar		BO = $\frac{4}{3}$ = 1.33
Nitronium ion (NO_2^+)	(sp) + 0 lp linear		BO = 2

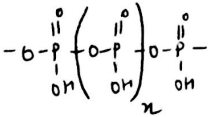
B.O of $NO_2^+ > NO_2^- > NO_3^-$

B.L of $NO_2^+ < NO_2^- < NO_3^-$

2. Oxo acids of P

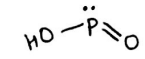
Oxo acid name	Formula	Structure	Prep	Imp. aspects
1. Hypo phosphorus acid	H_3PO_2		• $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaHPO_2 + PH_3$ $NaH_2PO_2 + HCl_{(dil)} \longrightarrow \boxed{H_3PO_2} + NaCl$	• Basicity = 1 • Types of salts = 1 (Only normal) Ex: NaH_2PO_2 • Reducing agent: $H_3PO_2 + AgNO_3 + H_2O \rightarrow Ag\downarrow + H_3PO_4 + HNO_3$
2. Ortho phosphorus acid (or) phosphorous acid	H_3PO_3		• $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$	• B = 2 • S = 2 (Acidic & normal) Ex: NaH_2PO_3, Na_2HPO_3 • $H_3PO_3 \xrightarrow{\Delta} PH_3 + H_3PO_4$
3. Ortho phosphoric acid	H_3PO_4		• $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$	• B = 2 • S = 3 (2 Acidic & 1 normal) NaH_2PO_4 – 1° phosphate (removing 1 H) Na_2HPO_4 – 2° phosphate Na_3PO_4 – 3° phosphate
4. Peroxy phosphoric acid	H_3PO_5		• $P_4O_{10} + 2H_2O + 4H_2O_2 \longrightarrow 4H_3PO_5$	• B = 3 • Unstable so no salts

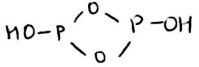
Oxo acid name	Formula	Structure	Prep	Imp aspects
5. Pyro phosphorous acid	$H_4P_2O_5$	 $p^3 - p^3$	• $5H_3PO_3 + PCl_3 \longrightarrow 3H_4P_2O_5 + 3HCl$	• B = 2 • S = 2
6. Pyro phosphoric acid	$H_4P_2O_7$	 $p^5 - p^5$	• $2H_3PO_4 \xrightarrow[-H_2O]{520K} H_4P_2O_7$	• B = 4 • S = 4
7. Hypo phosphoric acid	$H_4P_2O_6$	 $p^4 - p^4$	• $2P + 4NaOH + 2H_2O \longrightarrow H_4P_2O_6 + 4NaH$ (RED) (H_2 + NaOH)	• B = 4 • S = 4
8. Meta phosphoric acid (Glacial phosphoric acid)	HPO_3 (sp^2)		• $H_3PO_4 \xrightarrow[-H_2O]{520K} H_4P_2O_7 \xrightarrow[-H_2O]{870K} HPO_3$	• Exists as polymer • Glacial phosphoric acid (ice like crystals)
9. Cyclic trimeta phosphoric acid	$(HPO_3)_3$	 $(P_3)^5$	• $3H_3PO_3 + Br_2 \xrightarrow[(Br_2\text{-water})]{H_2O} (HPO_3)_3 + 6HBr$	• B = 3

Vo: Poly meta phosphoric acid	$(HPO_3)_n$		• $H_3PO_4 \xrightarrow[\text{heating}]{\text{strong}} (HPO_3)_n$	• Poly basic acid • Graham's salt (or) Calgon $(NaPO_3)_6 \equiv Na_2[Na_4(PO_3)_6]$

- Meta phosphorous acid
  (HPO_2)

  Exists as polymer



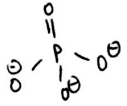


Dimer

- In all oxo acids of phosphorous (except HPO_2, HPO_3), central atom P is in sp^3 hybridised state.
  ∴ The $p\pi$ bonds are $p\pi-d\pi$ bonds

- Anhydride of $H_3PO_3 = P_4O_6$
  $H_3PO_4 = P_4O_{10}$

- Fractional charge on Oxygen in $PO_4^{3-} = \left(\frac{-3}{4}\right)$



- $H_3PO_3 \xrightarrow{\Delta} PH_3 + H_3PO_4$
- $H_3PO_2 + AgNO_3 + H_2O \longrightarrow Ag\downarrow + H_3PO_4 + HNO_3$

- Oxo acids of P containing H that are directly bonded to P act as reducing agents.

Ex: H_3PO_2 , H_3PO_3 , $H_4P_2O_5$

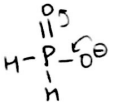
- **Reducing power ∝ No. of P-H bonds**

∴ Reducing power of H_3PO_2 > H_3PO_3 > H_3PO_4

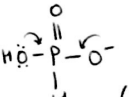
H_3PO_2: 2 (P-H) bonds; H_3PO_3: 1 (P-H) bond; H_3PO_4: 0 (P-H) bonds

*

- Acidic strength of H_3PO_2 > H_3PO_3 > H_3PO_4 (K_{a_1})

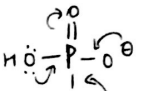


$(H_2PO_2^-)$



$(H_2PO_3^-)$

cross conjugation



$(H_2PO_4^-)$

More cross conjugation

Resonance stabilization

- H_3PO_4 ($K_{a_1} = 10^{-3}$: $K_{a_2} = 10^{-8}$: $K_{a_3} = 10^{-12}$)

i) Aq. NaH_2PO_4 $\quad pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{3+8}{2} = 5.5$ — Aq. soln is acidic

ii) Aq. Na_2HPO_4 $\quad pH = \frac{pK_{a_2} + pK_{a_3}}{2} = \frac{8+12}{2} = 10$ — Aq. soln is basic

iii) Aq. Na_3PO_4 $\quad pH = 7 + \frac{1}{2}[pK_{a_2} + \log c]$

$\simeq 7 + \frac{1}{2} \times 12$

$\simeq 13$

Aq. soln is basic

H_3PO_3 ($ka_1 = 10^{-2}$, $ka_2 = 10^{-7}$)

Aq. NaH_2PO_3 $\quad pH = \frac{pka_1 + pka_2}{2} = \frac{2+7}{2} = 4.5$ $\quad$ Aq. soln is acidic

Aq. Na_2HPO_3 $\quad pH = 7 + \frac{1}{2}[pka_2 + \log c]$

$= 7 + \frac{1}{2}(7)$

$= 10.5$ $\quad$ Aq. soln is basic

Nitrogen

- Colourless, Odourless
- BP = 77.2 K $\quad$ (B.P of O_2 = 90 K)
- FP = 63.2K
- Solubility = 23.2mL per litre at 298 K and 1 atm
- Solubility of $N_2 > O_2$ $\quad$ (~~since~~ easily liquefiable gases are more soluble but it also depends on K_H)

$P = K_H \times gas$

Prep:

1. $2NaN_3 \longrightarrow 2Na + \boxed{3N_2 \text{ pure}}$

$Ba(N_3)_2 \longrightarrow Ba + \boxed{3N_2 \text{ pure}}$

Pure N_2 obtained by decomposition of azides

2. $NaNO_2 + NH_4Cl \longrightarrow NH_4NO_2 + NaCl$

$\downarrow$

$N_2 + 2H_2O$

3. $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3$ (green) $+ 4H_2O$

4. $2NH_3 + CuO \longrightarrow N_2 + 3Cu + 3H_2O$

5. $NaNO_2 + NH_2CONH_2$ (urea) $\longrightarrow N_2 + Na_2CO_3 + H_2O$

$NH_2CONH_2 + HNO_2 \longrightarrow N_2$

6. $NH_4^+ +$ oxidising anion (NO_2^-, NO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, ClO_4^-) $\xrightarrow{\Delta} N_2/N_2O$

$NH_4^+ +$ Non-oxidising anion (Cl^-, Br^-, I^-, SO_4^{2-}, CO_3^{2-}) $\xrightarrow{\Delta} NH_3$

Uses:

- Creating inert atmosphere
- Refrigerant
- Preservation of food materials.

Ammonia

- Colourless, pungent smelling gas
- BP = 239.8K
- FP = 198.5 K
- Highly soluble in H_2O

- Levelling solvent (due to self ionization / auto protolysis)

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

- Liquor ammonia bottles are cooled before opening lid.

Reason: NH_3 has high vapour pressure at room temp. when lid is opened under high pressure, the liquid may rush out of the bottle.

- Poisonous.

Prep:

1. $NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$

NH_4Cl, NH_4Br, NH_4I, $(NH_4)_2SO_4$ $\xrightarrow{\Delta} NH_3$

Non-oxidising anions

2. NH_4^+-salt + Alkali $\xrightarrow{\Delta} NH_3$

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

$$(NH_4)_2SO_4 + CaO \longrightarrow CaSO_4 + 2NH_3 + H_2O$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

3. $Na + NH_4Br \longrightarrow NaBr + NH_3 + \frac{1}{2}H_2$

4. $AlN + H_2O \longrightarrow Al(OH)_3 + NH_3$ (Serpeck's process)

Purification of white bauxite

$$Mg_3N_2 + H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

5. $Mg(NH_4)PO_4 \xrightarrow{\Delta} NH_3 + Mg_2P_2O_7 + H_2O$

(white crystalline) ppt

$NA(NH_4)HPO_4 \cdot 4H_2O \xrightarrow{\Delta} NH_3 + NaPO_3 + H_2O$

Microcosmic salt

Manufacture

1- Cyanamide process

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CaO + C \longrightarrow CaC_2 + CO\uparrow$

$CaC_2 + N_2 \longrightarrow \boxed{CaCN_2 + C}$

calcium cyanamide (graphite)

or

$CaNCN$

nitrolim (nitrogenous fertilizer)

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

$BaC_2 + N_2 \rightarrow Ba(CN)_2$

$CaCN_2 + 3H_2O \longrightarrow 2NH_3 + CaCO_3$

(steam)

2. Haber's process

Principle eq: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H = -92$ kJ

Enthalpy of formation of $NH_3 = -\frac{92}{2} = -46$ kJ/mol

Optimum high pressure = 200-400 atm

optimum low temp. = 725-775 K

Catalyst = Fe_3O_4 reduced to (Fe) activated - Finely divided Fe

Promoter = Mo (or) $(K_2O + Al_2O_3)$

3. $NaNH_2 + NH_4Cl \longrightarrow NaCl + 2NH_3$

Chemical properties

1. $2NH_3 + \frac{5}{2}O_2 \xrightarrow[\Delta]{Pt/Ir} 2\boxed{NO} + 3H_2O$

2. $NH_3 + CuO \xrightarrow{\Delta} \boxed{N_2} + Cu + H_2O$

3. $NH_3 + NaOCl \longrightarrow NaOH + NH_2Cl$ (very fast) — Raschig's method

$NH_2Cl + 2NH_3 \longrightarrow \boxed{N_2H_4} + NH_4Cl$ (slow)

hydrazine

$NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl$

4. $NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$
(excess)

$8NH_3 + 3Cl_2 \longrightarrow 4N_2 + 6NH_4Cl$
(excess)

$NH_3 + 3F_2 \longrightarrow NF_3 + 3HF$
(excess)

$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$
(excess)

Uses:

- Refridgerant
- Levelling solvent

* Due to the levelling effect of NH_3, CH_3COOH undergoes complete ionization, and hence behaves as strong acid

- Nitrogenous fertilizers & HNO_3 manufacture.
- $\boxed{NH_4NO_3 + Al}$ → Ammonal – Explosive (used in dynamite)
- NH_3 should not be dried by anh. $CaCl_2$, conc. H_2SO_4, P_4O_{10}

Reason: They react with NH_3

- $CaCl_2 + 4NH_3 \longrightarrow CaCl_2 \cdot 4NH_3$
- $H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$
- $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

- $H_3PO_4 + 3NH_3 \longrightarrow (NH_4)_3PO_4$

* NH_3 is dried only over CaO (quick lime)

Hydrazine

- Colourless, fuming liquid
- Undergoes combustion.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O \quad ; \Delta H = -629 \text{ kJ/mol}$$

$(N_2O_4$ (oxidant) + $MeNH-NH_2$ + $MeN-NH_2)$ $\longrightarrow$ Rocket fuel
(Methyl derivatives)

- Forms two series of salts.

$$NH_2-NH_2 + H^+ \longrightarrow NH_2-NH_3^+ \equiv (N_2H_5)^+$$

$$NH_2-NH_2 + 2H^+ \longrightarrow NH_3^+-NH_3^+ \equiv (N_2H_6)^{2+}$$

- N_2H_4 is a reducing agent.

$$N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$$

$$N_2H_4 + 2O_2 \longrightarrow 2H_2O_2 + N_2$$

$$N_2H_4 + 2CuSO_4 \longrightarrow 2Cu + 2H_2SO_4 + N_2$$

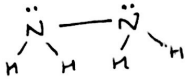
N_2H_4 acts as weak reducing agent in <u>acid med.</u>

- strong reducing agents can reduce N_2H_4 to NH_3

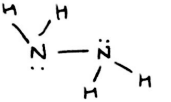
$N_2H_4 + Zn + HCl \longrightarrow NH_3 + ZnCl_2$

- $N_2H_4 + H_2O_2 \longrightarrow HNO_2$

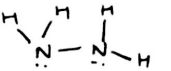
Conformations of N_2H_4



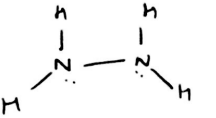
Fully eclipsed



Staggered



Gauche



Partially eclipsed

Hydroxyl amine

- Crystalline solid
- MP = 33°C
- Thermally unstable

$$NH_2OH \xrightarrow{\Delta} N_2 + N_2O + NH_3 + HNO_3$$

- $NH_2OH + HCl \longrightarrow [NH_2OH\,H]^+ Cl^-$
- $NH_2OH + H_2SO_4 \longrightarrow [NH_2OH\,H^+]\,HSO_4^-$
- Decomposition in acid med (of salts) – slow

$[NH_2OH\,H^+] \longrightarrow N_2O + NH_4^+ + H^+ + H_2O$

- Salt decomposition in alkaline med – rapid

$[NH_2OH\,H^+] \longrightarrow N_2 + NH_3 + H_2O$

- $NH_2OH + H_2O_2 \longrightarrow HNO_3$

  $N_2H_4 + H_2O_2 \longrightarrow HNO_2$

Hydrazoic Acid

- Colourless liquid
- BP = 37°C
- Thermally unstable & explodes in liquid & gas

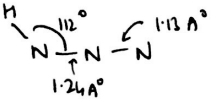
$$2N_3H \longrightarrow 3N_2 + H_2$$

- Equally acidic as CH_3COOH ($pk_a = 5$)

Prep:

*. $NaNH_2 + N_2O \longrightarrow NaN_3 + NH_3 + NaOH$

$2NaN_3 + H_2SO_4 \text{ (dil)} \longrightarrow 2HN_3 + Na_2SO_4$

- 

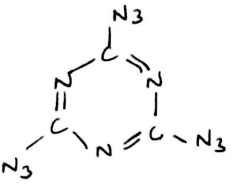
- Ionic azides are stable – used to make dye stuffs

  Covalent azides - detonate / explosive

$$Pb(NO_3)_2 + 2NaN_3 \longrightarrow \underset{\substack{\text{covalent}\\ \text{azide}}}{Pb(N_3)_2} + 2NaNO_3$$

Explodes

- Cyanuric acid is powerful explosive



* Azide ion (N_3^-) is pseudohalide.

Nitric acid

- Pure HNO_3 is colourless
- Yellow colour of HNO_3 is due to dissolved NO_2
- BP = 355.6 K
- MP = 231.4 K
- Density = 1.504 g/cc
- * $2HNO_3 \xrightarrow{\Delta} 2NO_2 + \frac{1}{2}O_2 + H_2O$
- Nitration mixture = 1:1 mixture of conc. HNO_3 + conc. H_2SO_4

$H\text{-}O\text{-}NO_2 + H_2SO_4 \longrightarrow H_2\overset{+}{O}\text{-}NO_2$

(Bronsted) base

- Aquaregia = 1:3 mixture of conc HNO_3 & conc HCl

$HNO_3 + 3HCl \longrightarrow NOCl + 2(Cl) + 2H_2O$

- Au, Pt, Ir, Rh are noble metals. They are insoluble in conc. HNO_3 but soluble in aquaregia

- $Au + 3(Cl) \rightarrow AuCl_3$

  $HCl + AuCl_3 \rightarrow H[AuCl_4]$

- $Pt + 4(Cl) \rightarrow PtCl_4$

  $PtCl_4 + 2HCl \rightarrow H_2[PtCl_6]$

- Metals that become passive with conc HNO_3 - **Al, Cr, Fe, Co, Ni**

- Fuming nitric acid - HNO_3 containing dissolved NO_2.

*

- Conc. nitric acid interacts with skin developing yellow colouration due to formation of **xanthoproteins**

Manufacture:

1. Ostwald's process:

$$2NH_3 + \frac{5}{2}O_2 \xrightarrow[850\ K,\ 9\ atm]{Pt/Rh} 2NO + 3H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + O_2 + H_2O \rightarrow 2HNO_3$$

2. Berkaand - Eyde process

$$N_2 + O_2 \xrightarrow{\text{Electric arc}} 2NO$$

(Air)

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

HNO_2 → $HNO_3 + NO + H_2O$

HNO_2 → $NO + NO_2 + H_2O$

Concentration of HNO_3:

Aq. HNO_3 $\xrightarrow{\text{Fractional Distillation}}$ 68% HNO_3 $\xrightarrow[H_2SO_4]{\text{conc.}}$ 90% HNO_3 $\xrightarrow{\text{crystallized}}$ 100% HNO_3

- Azeotropic mixture = (68% HNO_3 + 32% H_2O)

Chemical properties

1. Oxidising properties of HNO_3:

- HNO_3 while acting as oxidant gets reduced to NO_2 ~~(and rarely NO)~~

- HNO_3 (conc) oxidises:

$C \longrightarrow CO_2$

$S \longrightarrow H_2SO_4$

$SO_2 \longrightarrow H_2SO_4$

$H_2S \longrightarrow S$

$I_2 \longrightarrow HIO_3$

$Hg \longrightarrow Hg_2$

$HBr \longrightarrow Br_2$

$Fe^{+2} \longrightarrow Fe^{+3}$

$Sn \longrightarrow H_2SnO_3$

$Sb \longrightarrow H_3SbO_4$

$P \longrightarrow H_3PO_4$

$As \longrightarrow H_3AsO_4$

***

Sucrose to oxalic acid

$$C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow 6H_2C_2O_4 + 36NO_2 + 23H_2O$$

(0) → (+3), $3 \times 12 = 36$

***

$$KI + HNO_3 \longrightarrow KNO_3 + \boxed{NO} + H_2O + I_2$$

HNO_3 reduced to NO

$$Zn + \text{very dil. } HNO_3 \longrightarrow Zn(NO_3)_2 + NH_4NO_3$$

$$Zn + \text{dil. } HNO_3 \longrightarrow Zn(NO_3)_2 + N_2O$$

$$Zn + \text{conc. } HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2$$

} Even Fe reacts the same way

$$Cu + \text{dil. } HNO_3 \longrightarrow Cu(NO_3)_2 + NO$$

$$Cu + \text{conc. } HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2$$

Extremely dil. (2%)	Mg, Mn	Metal nitrate + H_2
Very dil (6%)	Fe, Zn, Sn	Metal nitrate + NH_4NO_3 + H_2O
Dilute (20%)	Pb, Cu, Ag, Hg	Metal nitrate + NO + H_2O
	Fe, Zn	Metal nitrate + N_2O + H_2O
	Sn	NH_4NO_3 + $Sn(NO_3)_2$
Conc. (70%)	Fe, Zn, Pb, Cu, Ag	Metal nitrate + NO_2 + H_2O
	Sn	H_2SnO_3 + NO_2

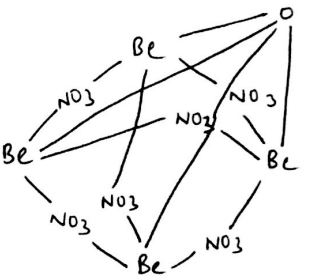
- $NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$

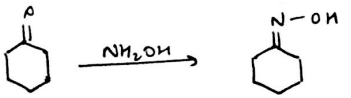
Uses:

- Explosives & ~~pyrotechnics~~
- Manufacture of TNT, nitroglycerine & other explosives
- Pickling agent (Removing rust)
- Etching of metals
- Oxidiser in rocket fuels

- $BeCl_2 + N_2O_4 \xrightarrow{\Delta} Be(NO_3)_2 \cdot 2N_2O_4 \xrightarrow[\text{vacuum}]{50^\circ} Be(NO_3)_2 \xrightarrow{125^\circ C} [Be_4O(NO_3)_6]$ Basic beryllium nitrate + N_2O_5



~~Phosphorous~~

- 

Acid
Any LA (BF_3, PCl_5)
HCl
Beckmann's rearrangement

Polymerization → Caprolactum (Nylon-6)

$-(HN-CO-CH_2CH_2CH_2CH_2CH_2)_n-$
6-carbons

Phosphorous

Phosphine

- Colourless gas with rotten fish smell
- Toxic
- Sparingly soluble in water
- * Solution of PH_3 in water in the presence of sunlight decomposes into red P & H_2
- PH_3 is non-inflammable but it catches fire spontaneously due to presence of P_2H_4 (or) P_4 (white) vapours.
- PH_3 is made free from other gases by passing through a soln. of HI

$$PH_3 + HI \longrightarrow PH_4I$$

$$PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$$

- P_2H_4 (diphosphine) burns in air giving vortex rings

$PH_3 + P_2H_4$

and hence used in smoke screens.

$$P_2H_4 + \frac{7}{2}O_2 \longrightarrow 2HPO_3 + H_2O$$

- Holmes signal ($Ca_3P_2 + CaC_2$) (used in ships as SOS signal)

$$Ca_3P_2 + H_2O \longrightarrow PH_3\ (P_2H_4) + Ca(OH)_2$$

(PH_3 is almost always accompanied by P_2H_4)

$$CaC_2 + H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

- P_2H_4 spontaneously catches fire and ignites C_2H_2 which serves as signal.

Prep:

- $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
- $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$
- $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

Chemical properties

- PH_3 is a reducing agent.

$AgNO_3 + PH_3 \longrightarrow Ag_3P + HNO_3$

$HgCl_2 + PH_3 \longrightarrow Hg_3P_2 + HCl$

- $PH_3 + HX \longrightarrow PH_4X \quad (X = Cl, Br, I)$
- $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$ (excess)

Super phosphate of lime / Calcium superphosphate

- It is a primary phosphate
- Composition:

$[Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 \cdot 2H_2O]$

Calcium dihydrogen Phosphate (Soluble) — Gypsum (Insoluble)

Prep:

$$Ca_3(PO_4)_2 \underset{\text{(Finely divided) Phosphorite}}{} + \underset{\text{(Conc) (Chamber) acid}}{H_2SO_4} + H_2O \longrightarrow \left(Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 \cdot 2H_2O \right)$$

Impurities in phosphorite $CaCO_3$ & CaF_2

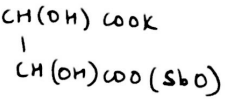
$$CaCO_3 \xrightarrow{H_2SO_4} CO_2 \uparrow$$

$$CaF_2 \xrightarrow{H_2SO_4} HF \uparrow$$

- It is not a completely soluble fertilizer due to gypsum
- It is a phosphatic fertilizer.
- When phosphorite rock is treated with H_3PO_4, a completely soluble fertilizer, triple phosphate is formed

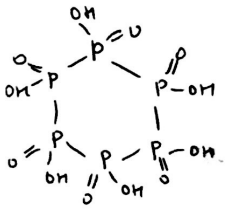
$$\underset{\text{phosphorite}}{Ca_3(PO_4)_2} + H_3PO_4 + H_2O \longrightarrow \underset{\text{(triple phosphate)}}{3Ca(H_2PO_4)_2 \cdot H_2O}$$

- CAN – Calcium ammonium nitrate (~~oddly~~ is hygroscopic
- Nitrogeneous fertilizer – non explosive
- Swart's reagent – SbF_3
- Tartar emetic –



It is used in medicine

- Ammonal – $NH_4NO_3 + Al$
- Amatol – 80% NH_4NO_3 + 20% TNT
- Scheele's green – $CuHAsO_3$
- Graham's salt – $(NaPO_3)_6$
- Paris green – $(CH_3COO)_2Cu \cdot 3Cu(AsO_2)_2$
- Pearl of white – $BiOCl$
- Nitrophos – $Ca(NO_3)_2$



$(P_6)^3$

$$2NH_3 + CO_2 \xrightarrow{200\ atm} NH_2COONH_4 \longrightarrow NH_2CONH_2 + H_2O$$

$$4PCl_3 + 6MeNH_2 \longrightarrow [P_2(NMeP)_3]_2 + 12HCl$$

- Azeotropic composition:

  $HNO_3 \rightarrow$ 68%.

  $H_2SO_4 \rightarrow$ 98%.

  $HCl \rightarrow$ 20.5%.

- In N_2H_4, N–N bond length is longer than expected due to repulsions of lone pairs.